

“On the Colouration of Glass by Natural Solar and other Radiations.” By Sir WILLIAM CROOKES, D.Sc., F.R.S. Received January 17,—Read January 26, 1905.

It is well known that many samples of colourless glass containing manganese slowly assume a violet tint when exposed to sunlight. This effect is frequently seen in plate-glass windows having a southern aspect; watched from year to year they assume a more and more pronounced amethystine hue. The introduction of manganese into glass is to neutralise the colour caused by the presence of iron. Iron gives the glass a greenish tint, and the addition of manganese binoxide performs the double object of oxidising the green proto-salt of iron to the per-salt, and also of imparting a purple shade which neutralises the green-yellow tint of the silicate of peroxide of iron.

In 1903, I received from two separate correspondents specimens of glass coloured an intense purple. I quote the following sentences from the covering letters:—

Mr. A. Ernest Williams writes:—

“While residing at Uyuni, in Bolivia, last year, at an altitude of nearly 4000 metres, my attention was called to the fact that all transparent white glass when thrown out on the ‘Pampa’ in a short time assumes a violet hue, which becomes more marked with time. I was told that all specimens were thus affected, and that when taken to sea level at Antofagasta they lost their colour. This latter statement I hardly believe, as I have had some pieces with me now on low level for nearly a year, and they have not lost the colour.

“I now notice that all transparent white glass thrown on rubbish heaps, even at low level, assumes this violet colour, though only to a slight degree, and I am curious to know the cause, being more interested since reading that radium so affects glass.

“I may mention that Uyuni is situated on the great central plain of Bolivia, which plain has evidently formed the bed of an inland sea or lake, for I have found quantities of minute shells there. Not far off to the south and south-west are borax fields, and still further west, nitrate. To the north-east are the mountains of Pulacayo and Cuzco (not the great Cuzco), and electrical disturbances are of almost daily occurrence. I can fully confirm Sir Martin Conway’s description of the battles between the mountains, where lateral discharges are plainly visible. I am sending you by post a small specimen of the glass.”

About the same time I received some specimens of purple-coloured glass from Mr. Thomas Wilson, from Iquique, Chile. In a subsequent letter answering some enquiries, he sent a further quantity of the coloured glass, saying:—

“You will notice a great variety in the depth or degree of tint in the

different pieces, which may be attributable to the varied length of the exposure of each to the action of the sun's rays. It seems to me that some of the pieces have lost somewhat of their depth of colour since I picked them up, but this may be an impression only. The two pieces forming together the bottom of a broken tumbler, and which have a deeper tint than any of the rest, were found about twenty paces apart in an old Oficina that had been uninhabited for 27 years. It is impossible to give any idea of the length of exposure of the remaining pieces to the sun's rays, as I have obtained them from all parts of the Pampa over an extent of nearly 100 miles. The samples I send you were originally white glass, and although an abundance of glass of various colours is to be found, yet I send you none, as it would not be easy to say what the original colours had been previous to exposure."

The pieces of glass referred to above are of all depths of tint, from deep violet, almost black in thick pieces, to pale amethyst. Analysis shows the glass to contain manganese. Heating the glass in a covered crucible to its softening point, discharges the colour, leaving the glass white and transparent.

The colouration is not superficial. On immersing a piece of the coloured glass in a liquid of about the same refractive index as itself, the colour is seen to have penetrated throughout the mass.

At first sight the explanation of this phenomenon would seem to be that it is produced by the action of light, the intense radiation occasioning a re-arrangement of the oxygen molecules in the glass, the ferric salt becoming ferrous, and the manganous salt changing to a manganic compound.* The change of colour might then be expected to be noticed in any part of the world where broken glass is thrown about and the sun's rays are very intense. In the Transvaal, where both these conditions are well fulfilled, I have neither heard of nor noticed any such colouration, and it would be interesting to hear if travellers in other tropical countries have observed any such change of colour of glass.

Probably height above sea level has much to do with the phenomenon. At a height of 4000 metres nearly half the atmosphere is beneath one's feet, and that which remains will allow rays of shorter wave-length to pass through than the atmosphere at sea level will transmit.

For this reason it is not necessary to invoke another mode of explanation that might possibly suggest itself. It now has been well established that many natural bodies, water from great depths, some samples of earth and rock, air from underground sources, together with some minerals, are more or less radio-active. Radium, acting for a few

* In this connection it may be of interest to recall the fact that in the early days of photographic research the ultra-violet rays of the spectrum were called the "deoxidising rays."

days, even through quartz, will produce as intense a colouration in a piece of this glass as exposure to the sun on the Pampa has taken years to effect. It is hardly conceivable that there can be a special radio-activity of the soil in certain parts of Chile and Bolivia sufficiently powerful to produce the effect.

A piece of the coloured glass, bleached by heat, was put close to a quartz tube in which about 15 milligrammes of pure radium bromide was sealed up. In the course of a few hours a faint amethystine tint could be distinguished on the glass, and in a week the tint was equal to the deep colour of the unbleached specimen. A duplicate piece of the same glass which had been bleached by heat, kept away from radium, remained colourless for seven weeks.

A piece of the deepest purple-coloured glass was put on a sensitive photographic film, and kept in the dark in contact with it for 34 days. No trace of action could be detected on developing.

The purple glass which had been bleached by heat and then coloured purple again by radium, was put in close contact with a sensitive film for 24 hours. On developing, no trace of action could be seen.

The darkening effect produced by radium on bodies exposed to its emanations is very general. Quartz, mica, glass of all kinds, and the diamond may be specially mentioned. In a paper recently read before the Royal Society "On the Action of Radium Emanations on Diamond,"* I showed that the β -rays (electrons) and γ -rays not only effected a superficial darkening, converting the surface of the diamond into graphite, but the body colour of the stone was changed from pale yellowish-brown to bluish-green; and I suggested the explanation that the action might be chemical, the ferric state of the iron being reduced to the ferrous state, and the colour thereby changing from yellow to blue-green.

In the year 1855, I tried a series of experiments with a spectrum camera furnished with two quartz prisms and a quartz lens, with the object of ascertaining if the atmosphere exerted any absorptive action on the more refrangible rays of light. Photographs of the solar spectrum were found to reveal lines of higher and higher refrangibility the nearer they were taken to mid-day, and arguing from this I concluded that the "noon-day spectrum at midsummer ought to contain more and higher rays than are possessed by the corresponding spectra at any other time of the year." The examination of the photographed spectra was continued through the summer, photographs being taken at noon whenever the sun was clear, and I found that "as the light came less obliquely through the atmosphere, new rays began to be apparent, until at midsummer, when the sun was on the meridian, I succeeded in obtaining evidence of the existence of rays which the most prolonged exposure failed to detect at any other time."

* 'Roy. Soc. Proc.,' June, 1904, vol. 74, p. 47.

I may perhaps be pardoned for quoting from my paper on the subject the following passage, written 50 years ago.*

“Some curious speculations arise from these facts. Should we be able, by working under a vertical sun, and with every advantage of cloudless sky, etc., to increase still more the length of our spectrum? Can we attain the limit of solar refrangible rays in this direction? Or is it not more likely that there are emanating from the sun torrents of rays which never approach the earth—rays which, beating against the upper stratum of the atmosphere, are themselves destroyed, but whose vibrative energy is transmitted to us with increased wave-length and lowered refrangibility, in the form of heat or light?”

Sunlight and radium both produce similar effects in these respects. Their modes of action are known to be in the main very different; but it has been clearly shown that, in general, variation of time being disregarded, what radium is capable of doing in the way of inducing chemical change, ionising gases, producing phosphorescence, and impressing a photographic plate, sunlight will also effect.

[*March 6.*—I am indebted to Professor McLeod for the following historical note on the action of light on glass:—“T. Gaffield, of Boston, U.S., ‘B.A. Report,’ 1872, Sect., pp. 37—38. Bontemps, ‘C.R.’ 69, 1869, 1075—1078; ‘Cosmos,’ 6, 1870, 66—75. In the ‘C.R., Bontemps presented to the Academy the results obtained by Gaffield, together with some of his own. He refers to the experiments of Faraday, which are described in ‘Quart Jl. Sci.,’ 19, 1825, 341. Faraday describes the change to violet which took place in certain glass after nine months’ exposure to sunlight in London, and mentions the colour of the window glass in houses in Blackfriars Bridge Road, now pulled down, but which I well remember. Bontemps also mentions work by Pelouze in 1867, described in ‘C.R.’ 64, pp. 53—66, in which he attributes the yellow colour, produced in some glass, to the formation of sulphides from the sodium sulphate by the action of ferrous oxide, an explanation which Bontemps thinks improbable.”

Professor Judd called attention, when the paper was read, to the deep colouration of the glass in the old greenhouses at Kew, in the parts where it has been exposed to light. Glass coloured green with oxide of iron for use in the forcing houses (as proposed by the late Robert Hunt) is found by long exposure to sunlight to gradually lose this colour and to become perfectly colourless. Subsequently a purple colour, due to small admixture of manganese in the original frit, makes its appearance. Visitors to the various houses in Kew Gardens can easily verify these facts for themselves, as the most varied tints, from green to colourless and purple, may be seen in different panes of glass, according to the period at which they have been put in during repairs.

* ‘Journal of the Photographic Society of London,’ vol. 2, p. 293.

Professor Judd has enabled me to try the action of radium emanations on specimens of this glass. Fifteen milligrammes of pure radium bromide sealed in a quartz tube were put close to a sample of the deepest green glass. In two days appreciable darkening took place, and in 10 days the darkening was very marked.

A similar experiment was tried on a sample of the purple-tinted glass; here also the action was the same as in the former case, and in 10 days the darkening was about the same. Allowing for the apparent alteration of colour caused by the initial tint of the two pieces of glass, I should say the colour produced by radium was similar in each case, and was of the same purple colour as that caused by long exposure to sunlight.]

“On the Comparison of the Platinum Scale of Temperature with the Normal Scale at Temperatures between 444° and -190° C., with Notes on Constant Temperatures below the Melting-point of Ice.” By MORRIS W. TRAVERS, D.Sc., F.R.S., and A. G. C. GWYER, B.Sc. Received January 11,—Read January 26, 1905.

Introduction.—During the last few years one of us has been engaged in researches involving the accurate measurement of low temperatures. The measurements were made by means of gas thermometers, of the constant volume type, filled with hydrogen, or with helium, at an initial pressure of 1000 mm. As, however, this method proved cumbrous and inconvenient, it was decided to standardise a platinum resistance thermometer of the Callendar type against the gas thermometer, and to employ it in future investigations. The comparison of the thermometers between -190° and 444° C. has been carried out with considerable accuracy, and as the range of temperature overlaps that investigated by Callendar and Griffiths, and by Harker and Chappuis, we have decided to publish our results, though from our own standpoint the work is only considered as preliminary to other investigations.

In expressing our results we have employed Callendar's notation. Thus, when R_0 is the resistance of a coil of platinum wire at the melting point of ice, and R_{100} is its resistance at the temperature of saturated steam under absolute standard pressure, which in the laboratory of University College, Bristol, is equivalent to 759.55 mm. of mercury at zero, the value of the coefficient of change of resistance, α , is given by

$$\frac{R_{100} - R_0}{100R_0} = \alpha.$$